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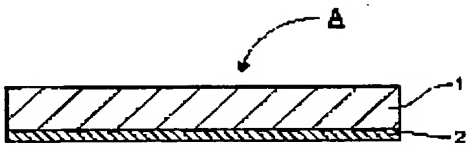
(54) BARRIER FILM AND LAMINATED MATERIAL USING THE SAME

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a barrier film having high barrier properties against oxygen gas, steam or the like, excellent in transparency and useful for packaging various articles, for example, food and drink, medicines, cosmetics, chemical products and the others, and a laminated material using the same.
SOLUTION: The barrier film is constituted by providing a membrane of an inorganic oxide due to a plasma chemical film forming method on one surface of a biaxially stretched polyamide resin film. The laminated material is obtained using this barrier film.



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CLAIMS

[Claim(s)]
[Claim 1] The barrier property film characterized by preparing the thin film of the inorganic oxide by the plasma chemistry forming-membranes method in one field of a biaxial drawing polyamide system resin film.
[Claim 2] The barrier property film indicated to above-mentioned claim 1 to which a biaxial drawing polyamide system resin film is characterized by carrying out dehydration processing before membrane formation of the thin film of an inorganic oxide.
[Claim 3] The barrier property film indicated to above-mentioned claims 1-2 to which a biaxial drawing polyamide system resin film is characterized by carrying out dehydration processing in vacuum oven.
[Claim 4] The barrier property film indicated to above-mentioned claims 1-2 to which a biaxial drawing polyamide system resin film is characterized by carrying out dehydration processing in the dry room of an absolute dry condition.
[Claim 5] The barrier property film indicated in the above-mentioned claim ports 1-4 where a biaxial drawing polyamide system resin film is characterized by being 0.3% - 0.7% (weight fraction) with the water content after dehydration processing before membrane formation of the thin film of an inorganic oxide.
[Claim 6] The barrier property film indicated to above-mentioned claims 1-5 characterized by the thin film of an inorganic oxide consisting of a thin film of the oxidization silicon by the plasma chemistry forming-membranes method.
[Claim 7] Plywood characterized by preparing a heat-sealing nature resin layer in the field of the thin film of the inorganic oxide which constitutes the barrier property film characterized by preparing the thin film of the inorganic oxide by the plasma chemistry forming-membranes method in one field of a biaxial drawing polyamide system resin film at least.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the plywood which used the barrier property film and it which are excellent in the gas barrier property to transparency, oxygen gas, or a steam etc., and have lamination fitness further in more detail about the plywood which used a barrier property film and it, for example, were excellent in the restoration package fitness over various articles, such as an eating-and-drinking article, drugs, cosmetics, a chemistry article, and others.
[0002]
[Description of the Prior Art] In order to carry out the restoration package of the various articles, such as an eating-and-drinking article, drugs, cosmetics, a chemistry article, and others, conventionally, the various raw materials for a package are developed and proposed. ** and as a barrier property raw material to oxygen gas or a steam in them in recent years On the front face of plastics base materials, such as a polyester system resin film or a polyamide system resin film Inorganic oxides, such as oxidation silicon, an aluminum oxide, a magnesium oxide, and others, are used. Physical vapor growth, such as vacuum evaporation technique, the sputtering method, and the ion plating method (PVD), Or the barrier property film which comes to form the vacuum evaporationo film of the inorganic oxide attracts attention using chemical-vapor-deposition methods (CVD method), such as plasma chemistry vapor growth, thermochemistry vapor growth, and photochemistry vapor growth, etc. It **, and the laminating of the above-mentioned barrier property film is carried out to other plastic films, a paper base, other raw materials, etc. and arbitration, various plywood is constituted, the container for a package useful for carrying out the restoration package of the various articles is manufactured, and amplification of the amount of need will be expected very much from now on. Especially the above-mentioned barrier property film is a raw material which it has the advantage which was excellent in incineration abolition processing proper **, and was excellent in versatility as a raw material which suits an environmental response, and attracts attention as compared with the barrier property raw material by the conventional aluminium foil or the polyvinylidene chloride system resin coat film.
[0003]
[Problem(s) to be Solved by the Invention] By the way, similarly in the above barrier property films, the polyamide system resin film as a base material film has the trouble that water absorption is very high, as compared with the polyester system resin film as a base material film etc. Usually, although a polyester system resin film hardly absorbs moisture, a polyamide system resin film has the trouble that saturation water absorption arrives at the bottom of the environment of 60% of relative humidity to about 4%, and has the trouble of absorbing more moisture under [of summer] highly humid especially. If it **, it faces manufacturing the above barrier property films and the above water absorption membrane-formation-izes as a base material film using a high polyamide system resin film, the slipping nature on the front face of a film will fall, for example, various troubles, like a film twines round the film piece by poor slipping and a roll in the case of film through will occur with roll-type chemical-vapor-deposition equipment. Furthermore, when water absorption membrane-formation-izes using a high polyamide system resin film, moisture floats and comes out from this polyamide system resin film in a vacuum pan, the degree of vacuum in a vacuum pan is reduced by this, and there is a trouble that it becomes difficult to manufacture the barrier property film excellent in the gas barrier property to oxygen gas, a steam, etc. Moreover, as mentioned above, if moisture etc. floats and comes out to the front face of the polyamide system resin film as a base material film Moisture occurs between a membrane formation drum and the polyamide system resin film as a base

material film. By this membrane formation drum lifting, a polyamide system resin film floats or Or the trouble that it becomes difficult for a wrinkle etc. to occur and to manufacture the barrier property film excellent in the gas barrier property to oxygen gas, a steam, etc. like the above by considering that as a cause is in a polyamide system resin film. Furthermore, if moisture etc. comes up to the front face of a polyamide system resin film as mentioned above again and a degree of vacuum etc. falls by that cause, the moisture from which the above came up at the time of membrane formation will advance into the vacuum evaporationo film of inorganic oxides, such as for example, oxidization silicon, and will influence the property of the vacuum evaporationo film, and it will lead to the trouble of causing lowering of the gas barrier property to the oxygen gas of the barrier property film obtained, a steam, etc. Moreover, when a polyamide system resin film floats by membrane formation drum lifting as mentioned above or a wrinkle etc. occurs on a polyamide system resin film, thereby, the plasma at the time of membrane formation becomes instability, phenomena, such as the so-called heat defeat, are caused and there is a trouble of causing lowering of the gas barrier property to the oxygen gas of the barrier property film obtained, a steam, etc.

[0004] For this reason, it sets on the above-mentioned barrier property film. In order to raise the gas barrier property to the oxygen gas or steam etc. for example, on the front face of the polyamide system resin film as a base material film, beforehand, carry out surface roughening of the front face by pretreating corona discharge treatment, glow discharge processing, etc., or Or beforehand, coat with anchor coat agents for vacuum evaporationo, such as an urethane system and an ester system, and an anchor coat agent layer is formed. Although the approach of raising gas barrier property by improving the adhesion of the polyamide system resin film as a base material film and the vacuum evaporationo film etc. is proposed Although the effectiveness by it can be expected as it is The actual condition is [which may fully be satisfied] that yes, it is difficult to manufacture the barrier property film which has barrier property, and further, if it adds, since performing such actuation itself and its production process increase, there is still a trouble of raising the manufacturing cost. The organic system anchor coat agent of a polyurethane system is used, beforehand, it coats with this on the front face of a polyamide system resin film, and an anchor coat agent layer is formed. For example, subsequently If the vacuum evaporationo film of an inorganic oxide is formed through this anchor coat agent layer, the degree of vacuum under vacuum evaporationo will fall for the residual solvent contained in an anchor coat agent layer. Further Since the anchor coat agent layer itself is soft, it sets on an anchor coat agent layer front face. It is very difficult for the vacuum evaporationo film not to grow well but to form the vacuum evaporationo film as a request, consequently the actual condition is being unable to manufacture the barrier wrapping material excellent in the gas barrier property to oxygen gas or a steam. Then, this invention is offering the plywood which has the high barrier property to oxygen gas or a steam, was excellent in transparency, for example, used a useful barrier property film and useful it for carrying out the restoration package of the various articles, such as an eating-and-drinking article, drugs, cosmetics, a chemistry article, and others.

[0005]

[Means for Solving the Problem] As a result of examining many things that this invention person should solve the above troubles, dehydration processing of the biaxial drawing polyamide system resin film is carried out before membrane formation of the thin film of an inorganic oxide, And the plasma chemistry forming-membranes method is rich in flexibility, flexibility, flattery nature, etc. in comparison. It notes being able to form the thin film of the inorganic oxide which can control generating of a crack etc. first a biaxial drawing polyamide system resin film For example, vacuum oven, Dehydration processing is carried out in the drying room of an absolute dry condition etc., and the water content after dehydration processing of a biaxial drawing polyamide system resin film is prepared to 0.3% - 0.7% (weight fraction) before membrane formation of the thin film of an inorganic oxide. Or subsequently To one field of this biaxial drawing polyamide system resin film, by the plasma chemistry forming-membranes method The thin film of inorganic oxides, such as oxidization silicon, is prepared, a barrier property film is manufactured, a heat-sealing nature resin layer etc. is further prepared in the thin film side of the inorganic oxide of this barrier property film at least, and plywood is manufactured. Subsequently This plywood is used, this is manufactured and the container for a package is manufactured. After an appropriate time, The place which carried out the restoration package of the contents into this container for a package, heat sealed the opening further, and manufactured the package object, Most phenomena in which moisture etc. comes up from a biaxial drawing polyamide system resin film at the time of membrane formation of the thin film of inorganic oxides, such as oxidation silicon, cannot be accepted. And the effect does not exist, either and the

thin film of inorganic oxides, such as oxidation silicon, can be membrane-formation-ized very good on the front face of this polyamide system resin film. And it excels in the adhesion of this biaxial drawing polyamide system resin film and the thin film of inorganic oxides, such as oxidation silicon. Consequently, it has the very high barrier property to oxygen gas or a steam. And it finds out that the plywood which was excellent in transparency, and was excellent in lamination reinforcement etc. further, for example, used a useful barrier property film and useful it for carrying out the restoration package of the various articles, such as an eating-and-drinking article, drugs, cosmetics, a chemistry article, and others, can be manufactured, and this invention is completed.

[0006] That is, this invention relates to the plywood which used the barrier property film and it which are characterized by preparing the thin film of the inorganic oxide by the plasma chemistry forming-membranes method in one field of a biaxial drawing polyamide system resin film.

[0007]

[Embodiment of the Invention] Above-mentioned this invention is explained in more detail below. When the 12 examples are illustrated and the configuration of the plywood which used the barrier property film and it concerning this invention is explained using a drawing, drawing 1 is the rough sectional view showing the lamination of the example about the barrier property film concerning this invention, and drawing 2 is the rough sectional view showing the lamination of the example about the plywood concerning this invention.

[0008] First, as shown in drawing 1 , the barrier property film A concerning this invention carries out dehydration processing in vacuum oven or the drying room of an absolute dry condition, and makes things basic structure from the configuration which formed the thin film 2 of the inorganic oxide by the plasma chemistry forming-membranes method in one [which prepared the water content after dehydration processing to 0.3% - 0.7% (weight fraction) before membrane formation of the thin film of an inorganic oxide] field of the biaxial drawing polyamide system resin film 1. As it ** and is shown in drawing 2 , as plywood B which used the barrier property film concerning this invention in this invention, as mentioned above For example, vacuum oven, Dehydration processing is carried out in the drying room of an absolute dry condition etc. or before membrane formation of the thin film of an inorganic oxide To one field of the biaxial drawing polyamide system resin film 1 prepared to 0.3% - 0.7% (weight fraction), the water content after dehydration processing If required for the field of the thin film 2 of the inorganic oxide of the barrier property film A which consists of a configuration of having formed the thin film 2 of the inorganic oxide by the plasma chemistry forming-membranes method, for example The adhesives layer for a lamination, Or things are made into basic structure at least through an anchor coat agent layer (not shown) etc. from the configuration which formed the heat-sealing nature resin layer 3. The above-mentioned instantiation illustrates the example and, thereby, this invention is not limited.

[0009] Next, manufacture of the barrier property film which will be applied to this invention if the manufacturing method is explained about the barrier property film concerning above this inventions in this invention A moisture-proof paper is removed from the biaxial drawing polyamide system resin film rolling-up original fabric film by which the sealing package is carried out with the moisture-proof paper etc. first, subsequently The rolling-up original fabric film temperature and 60 degrees C - about 90 degrees C A degree of vacuum, Put in into the vacuum oven prepared at least to 0.03mbar - 5 mbar, and [whether grade neglect is carried out for - two days during one day, and] Or at least temperature, and 25-degree-C60 degree C are put into a degree of vacuum, ordinary pressure, humidity, and the drying room prepared to 0% - about 20%. Grade neglect is carried out for - seven days during one day, dehydration processing is carried out and the biaxial drawing polyamide system resin film which prepared the water content after dehydration processing to 0.3% - 0.7% (weight fraction) before membrane formation of the thin film of an inorganic oxide is manufactured. In this invention, the biaxial drawing polyamide system resin film which carried out dehydration processing by the above is used, and the monomer gas for membrane formation, such as an organosilicon compound, is used as a raw material in the field of one of these. Next, this, Furthermore, adjust the mixed-gas constituent for oxygen gas and the membrane formation which contains inert gas, such as argon gas and gaseous helium, others, etc. further again, and this mixed-gas constituent for membrane formation is used. The thin film of inorganic oxides, such as oxidization silicon, can be formed using the plasma chemistry forming-membranes method (CVD method) for using a low-temperature plasma generator etc., and the barrier property film concerning this invention can be manufactured. In the above, in order to ** and for using generators, such as RF plasma, pulse wave plasma, and microwave plasma, to acquire **** and the plasma by which high activity was stabilized

in this invention as a low-temperature plasma generator, for example, it is desirable to use the generator by the RF plasma method.

[0010] In this invention, when the example is illustrated and explained about the manufacturing method of the barrier property film applied to this invention using the method of forming the thin film of the inorganic oxide by the above plasma chemistry forming-membranes methods, drawing 3 is the rough block diagram of the plasma chemistry membrane formation equipment in which the outline is shown about the method of forming the thin film of the inorganic oxide by the plasma chemistry forming-membranes method concerning this invention. In this invention, as shown in drawing 3 , first, it has been arranged in the vacuum chamber 12 of plasma chemistry membrane formation equipment 11, begins to wind, and lets out the biaxial drawing polyamide system resin film 1 from a roll 13. Next, in this invention, the biaxial drawing polyamide system resin film 1 which began to roll above and it let out from the roll 13 is conveyed on the membrane formation drum 15 peripheral surface which consists of cooling and an electrode drum at the rate of predetermined through Guy Delors 14 grade. In this invention Subsequently, from raw material volatilization feeder 18 grade to gas transfer units 16 and 17 and oxygen gas, The monomer gas for membrane formation, such as inert gas and an organosilicon compound, others, etc. are supplied. Adjust the mixed-gas constituent for membrane formation which consists of them, and the above-mentioned mixed-gas constituent for membrane formation is introduced in the vacuum chamber 12 through the inside feeding nozzle 19. On the front face of the above-mentioned biaxial drawing polyamide system resin film 1 conveyed on the membrane formation drum 15 peripheral surface which consists of the above-mentioned cooling and electrode drum, by the glow discharge plasma 20, the plasma is generated, this is irradiated and the thin film of inorganic oxides, such as oxidation silicon, is film-production-ized. In this invention, the membrane formation drum 15 which consists of cooling and an electrode drum in that case arranges a magnet 22 near the membrane formation drum 15 which predetermined power is impressed from the power source 21 arranged out of the vacuum chamber 12, and consists of cooling and an electrode drum, and generating of the plasma is promoted. Subsequently, in this invention, the biaxial drawing polyamide system resin film 1 which formed the thin film of inorganic oxides, such as oxidation silicon, above can be rolled round through Guy Delors 23 grade, it can roll round on a roll 24, and the barrier property film concerning this invention can be manufactured. In addition, 25 express a vacuum pump among drawing. It is a thing needless to say that it is not that to which the above-mentioned instantiation illustrates an example of the manufacturing method of the barrier property film concerning this invention, and this invention is limited by this.

[0011] In the above, the inside of the vacuum chamber 12 is decompressed with a vacuum pump 25, and it is desirable to prepare at least to degree of vacuum 1x10-3 - 1x10-7 mbar as preferably as degree of vacuum 1x10-1 - 1x10-8mbar. Moreover, in the raw material volatilization feeder 18, volatilize the organosilicon compound which is a raw material, it is made to mix with oxygen gas, inert gas, etc. which are supplied from gas transfer units 16 and 17, and this mixed gas is introduced in the vacuum chamber 12 through the feeding nozzle 19. In this case, about 1 to 40%, the content of oxygen gas can make the content of inert gas about 10 - 60% of range about 10 to 70%, for example, the content of the organosilicon compound in mixed gas can make the mixing ratio of an organosilicon compound, oxygen gas, and inert gas about 1:6:5-1:17:14. On the other hand to the membrane formation drum 15 which consists of cooling and an electrode drum Since the predetermined electrical potential difference is impressed from the power source 21, the glow discharge plasma 20 is generated near the membrane formation drum 15 which consists of opening of the feeding nozzle 19 in the vacuum chamber 12, and cooling and an electrode drum. This glow discharge plasma 20 is drawn from one or more gas constituents in mixed gas, and is set in this condition. The biaxial drawing polyamide system resin film 1 can be made to be able to convey with constant speed, and the thin film of inorganic oxides, such as oxidation silicon, can be formed on the biaxial drawing polyamide system resin film 1 on the membrane formation drum 15 peripheral surface which consists of cooling and an electrode drum by glow discharge PURABUMA 20. In addition, as for the degree of vacuum in the vacuum chamber at this time, it is desirable to prepare at least to degree of vacuum 1x10-1 - 1x10-2 mbar as preferably as 1x10-1 - 1x10-4mbar, and it is desirable 10-300m part grade for /and to prepare preferably the bearer rate of the biaxial drawing polyamide system resin film 1 at 50-150m part grade for /.

[0012] In above plasma chemistry vapor growth equipment 11 moreover, formation of the thin film of inorganic oxides, such as oxidation silicon It is SiOX, oxidizing the material gas plasma-ized on the biaxial drawing polyamide system resin film 1 with oxygen gas. Since it is formed in the shape of a thin

film in a form The thin film of inorganic oxides, such as the oxidation silicon concerned formed It is precise and is a thing used as the continuation layer which is rich in flexibility, flexibility, etc. with few clearances. Therefore, the barrier property of the thin film of inorganic oxides, such as oxidization silicon As compared with the vacuum evaporationo film of inorganic oxides, such as oxidation silicon formed by the conventional vacuum deposition method etc., it will become far high, and sufficient barrier property can be obtained by thin thickness. Moreover, it sets to this invention and is SiOX. Since the front face of the biaxial drawing polyamide system resin film 1 is defecated by the plasma and a polar group, a free radical, etc. are generated on the front face of the biaxial drawing polyamide system resin film 1, the close arrival nature of the thin film of inorganic oxides, such as oxidation silicon formed, and a biaxial drawing polyamide system resin film has the advantage of becoming high. As mentioned above furthermore, the degree of vacuum at the time of formation of the thin film of inorganic oxides, such as oxidation silicon At least 1x10-1 - 1x10-4mbar preferably The degree of vacuum when forming the vacuum evaporationo film of inorganic oxides, such as oxidation silicon, with the conventional vacuum deposition method from preparing at least to 1x10-1 - 1x10-2 mbar, By comparing at least with 1x10-4 - 1x10-5 mbar, since it is whenever [low-vacuum], the vacua setup time at the time of original fabric exchange of the biaxial drawing polyamide system resin film 1 can be shortened, it is easy to stabilize a degree of vacuum, and a film production process is stabilized.

[0013] In this invention, the thin film of inorganic oxides, such as oxidation silicon formed using vacuum evaporationo monomer gas, such as an organosilicon compound Vacuum evaporationo monomer gas, oxygen gas, etc., such as an organosilicon compound, react chemically. The resultant is the thin film of the letter of continuation which carries out close arrival to one field of a biaxial drawing polyamide system resin film, forms the thin film which is rich in precise flexibility, flexibility, etc., and usually makes a subject the oxidation silicon expressed with a general formula SiOX (however, X expresses the number of 0-2). It is desirable that it is the thin film which ** and makes a subject the continuation film of the oxidization silicon expressed with a general formula SiOX (however, X expresses the number of 1.3-1.9.) from points, such as transparency and barrier property, as a thin film of the above-mentioned oxidization silicon. In the above, although gas transmittance will become small if the value of X generally becomes small, although the value of X changes with the mole ratio of vacuum evaporationo monomer gas and oxygen gas, the energy of the plasma, etc., the film itself wears yellow nature and transparency worsens.

[0014] Moreover, the thin film of the above-mentioned oxidation silicon makes oxidation silicon a subject, and is characterized by consisting the compound which becomes this from one kind of carbon, hydrogen, silicon, or oxygen, or two or more kinds of its element further of continuation film contained by a chemical bond etc. in at least one kind. For example, when the compound which has C-H coupling, the compound which has Si-H association, or the carbon unit is the shape of the shape of the shape of graphite, and a diamond, and fullerene etc., the organosilicon compounds and those derivatives of a raw material may be further contained by a chemical bond etc. It is CH3 when an example is given. A hydrocarbon and SiH3 with a part Silyl and SiH2 Hydroxyl-group derivatives, such as hydro silicas, such as silylene, and a SiH2 OH silanol, etc. can be mentioned. Also except the above, the class of compound contained in the continuation film of oxidation silicon, an amount, etc. can be changed by changing the conditions of a vacuum evaporationo process etc. As a content which it ** and is contained in the continuation film of the oxidation silicon of the above-mentioned compound, about 0.1 to 50%, it is [about 5 - 20% of] desirable, and desirable. bending [content becomes inadequate / the shock resistance of the thin film of oxidation silicon, spread nature, flexibility etc. / for it to be less than 0.1%, and] in the above -- ** -- if it is alike, and it is easier to generate an abrasion, a crack, etc., and it becomes difficult for it to be stabilized and to maintain high barrier property and 50% is exceeded, barrier property falls and it is not desirable. In this invention, it is desirable in the thin film of oxidation silicon that the content of the above-mentioned compound makes it decrease toward the depth direction from the front face of the thin film of oxidation silicon. Furthermore, by this In the front face of the thin film of oxidation silicon, shock resistance etc. is raised by the above-mentioned compound etc. and it sets to an interface with another side and a biaxial drawing polyamide system resin film. Since there are few contents of the above-mentioned compound, the close arrival nature of a biaxial drawing polyamide system resin film and the thin film of oxidation silicon has the advantage of becoming firm.

[0015] It ** and the above physical properties can be checked from performing elemental analysis of the thin film of oxidation silicon using the approach of carrying out carrying out ion etching in the depth direction about the thin film of the above-mentioned oxidation silicon using surface analysis

equipments, such as for example, X-ray-photoelectron-spectroscopy equipment (Xray Photoelectron Spectroscopy, XPS) and secondary-ion-mass-spectroscopy equipment (Secondary Ion Mass Spectroscopy, SIMS), etc., and analyzing in this invention. In this invention moreover, as thickness of the thin film of the above-mentioned oxidation silicon It is desirable that it is only 50A - 4000A only of thickness. Specifically As the thickness, about 100-1000A ** by being desirable, and it sets above. 1000A further If it becomes thicker than 4000A, since it will become easy to generate a crack etc. on the film, it is not desirable, and it is not desirable from it becoming difficult to do so 100A of effectiveness of barrier property further, as it is less than 50A. The above can set and the thickness can be measured with a fundamental parameter method using the X-ray fluorescence equipment made from for example, incorporated company physical science (a model name, RIX2000 mold). Moreover, in the above, it can carry out by the approach of making [many] it to enlarge volume velocity of a thin film, i.e., monomer gas and the amount of oxygen gas, as a means to change the thickness of the thin film of the above-mentioned oxidation silicon, the approach of making late the rate to vapor-deposit, etc.

[0016] next, in the above, as monomer gas for vacuum evaporationo, such as an organosilicon compound which forms the thin film of inorganic oxides, such as oxidation silicon For example, 1.1.3.3-tetramethyl disiloxane, hexa methyl disiloxane, A vinyl trimethyl silane, a methyl trimethyl silane, a hexa methyl disilane, Methylsilane, dimethylsilane, a trimethyl silane, diethylsilane, A propyl silane, phenylsilane, vinyltriethoxysilane, vinyltrimetoxysilane, A tetramethoxy silane, a tetra-ethoxy silane, phenyltrimethoxysilane, methyl triethoxysilane, octamethylcyclotetrasiloxane, others, etc. can be used. In this invention, it is an especially desirable raw material to use 1.1.3.3-tetramethyl disiloxane or hexa methyl disiloxane as a raw material also in the above organosilicon compounds from the handling nature, the property of the formed continuation film, etc. Moreover, in the above, argon gas, gaseous helium, etc. can be used as inert gas, for example.

[0017] In above-mentioned this invention, as a biaxial drawing polyamide system resin film which constitutes a barrier property film, plywood, etc. concerning this invention, it excels in shock resistance, anti-stick property, etc., and is rich in tough nature, for example, and further, if it is the film thru/or sheet of biaxial drawing polyamide system resin which can hold the thin film of an inorganic oxide, anything can be used. Specifically, various kinds of film thru/or sheets of polyamide system resin (nylon), such as Nylon 46, nylon 6, Nylon 66, Nylon 610, Nylon 612, nylon 7, Nylon 11, Nylon 12, and others, can be used. It **. The above-mentioned film thru/or above-mentioned sheet of polyamide system resin (nylon) For example, a monolayer, or the thing which produced the film with the coextrusion process more than two-layer -- further -- for example, a tenter method -- Or it is desirable to use the film thru/or sheet of 1 - biaxial drawing polyamide system resin (nylon) which carried out drawing processing in the 1 - biaxial direction by the usual 1 - biaxial drawing approaches, such as a CHU-tenter method or a tubular method. Moreover, as the thickness, about 10-50 micrometers is desirable preferably about 5-200 micrometers. In addition, if the above-mentioned film thru/or above-mentioned sheet of biaxial drawing polyamide system resin is required, it can coat with an anchor coat agent etc., and can also perform surface data smoothing etc., and can perform surface treatment, such as corona discharge treatment, plasma electrodischarge treatment, ozonization, flame treatment, and others, to arbitration. In this invention, the plywood which has those properties can be manufactured using tough nature, such as reinforcement which it has, shock resistance, and anti-stick property, by using the film thru/or sheet of the above biaxial drawing polyamide system resin (nylon) as a base material. In addition, in this invention, the additive of requests, such as an antistatic agent, an ultraviolet ray absorbent, a plasticizer, lubricant, a bulking agent, and others, can be added to arbitration within limits which do not influence the transparency, corresponding to an application, and a film thru/or a sheet, etc. containing them of resin can be used.

[0018] Generally, a polyamide system resin film will have big effect, if water absorption nature is very large and forms membranes using the plasma chemistry forming-membranes method etc. as compared with other base materials for this reason. Most quantity of moisture is absorbed and especially a polyamide system resin film adsorbs, although water absorption nature is very large and is packing up the rolling-up original fabric film etc. with the moisture-proof paper etc. under [of summer] highly humid. About 1.5%, although it is the water content of a polyamide system resin film, when severe, it usually becomes about 35 from 1% about 2% under highly humid. Therefore, if such a polyamide system resin film is used and membranes are formed using the plasma chemistry forming-membranes method etc., the frequency where generating of the wrinkle of the film at the time of

barrier property lowering and membrane formation, a float, etc. increases summer, and the plasma becomes instability will be high, and it will become difficult to manufacture a desirable barrier property film. Moreover, in a winter season, although water content of instability [generating of the wrinkle of the film at the time of barrier property lowering and membrane formation, a float, etc.,] of the plasma decreases at about 1% as compared with summer, the actual condition is being what is not lost thoroughly. In view of the above situations, by performing dehydration processing, preparing the water content of a polyamide system resin film to 0.3% - 0.7%, and using this polyamide system resin film, generating of the wrinkle of the film at the time of membrane formation, a float, etc. can be abolished thoroughly, and adverse effects, such as stabilization of the plasma and others, are eliminated, and manufacture of a desirable barrier property film is enabled before membrane formation in this invention. When water content dries too much that it is less than 0.3% as a phenomenon unlike the original physical properties of a polyamide system resin film, and becomes lacking in the flexibility of a film in the above, and the film itself becomes easy to go out and it opens to atmospheric air after membrane formation, in order to absorb many moisture, it is not desirable from the problem which a film swells and a crack etc. produces in the thin film of an inorganic oxide occur. Moreover, if water content exceeds 0.7%, it is not desirable from the wrinkle of the film at the time of barrier property lowering and membrane formation, a float, etc. being generated, producing adverse effects, such as plasma instability and others, further, and manufacture of a desirable barrier property film becoming very difficult.

[0019] next, as heat-sealing nature resin which forms the heat-sealing nature resin layer which constitutes the plywood which used the barrier property film concerning this invention in this invention The film thru/or sheet of resin which fuses with heat and can be welded mutually can be used. Specifically For example, low density polyethylene, medium density polyethylene, high density polyethylene, Straight chain-like (line) low density polyethylene, polypropylene, an ethylene-vinylacetate copolymer, Ionomer resin, an ethylene-acrylic-acid copolymer, an ethylene-ethyl-acrylate copolymer, An ethylene-methacrylic-acid copolymer, an ethylene-methyl-methacrylate copolymer, Ethylene propylene rubber, methylpentene polymer, polybutene polymer -, Polyolefine system resin, such as polyethylene or polypropylene, an acrylic acid, The acid denaturation polyolefin resin which denaturalized with unsaturated carboxylic acid, such as a methacrylic acid, a maleic acid, a maleic anhydride, boletic acid, and an itaconic acid, The film thru/or sheets of resin, such as polyvinyl acetate system resin, Pori (meta) acrylic resin, polyvinyl chloride system resin, and others, can be used. It ** and an above-mentioned film thru/or an above-mentioned sheet can be used also in the state of the coating film by the constituent containing the resin. As thickness of the film or a film thru/or a sheet, 5 micrometers thru/or about 300 micrometers are desirable, and 10 micrometers thru/or about 100 micrometers are still more desirable.

[0020] In addition, in this invention, it is desirable to use the ethylene and the alpha olefin copolymer which carried out the polymerization, using a metallocene catalyst especially as heat-sealing nature resin which forms the above-mentioned heat-sealing nature resin layer. It ** and the ethylene-alpha olefin copolymer which comes to carry out a polymerization using the catalyst by the combination of 2 chlorination zirconocene, metallocene complexes, such as a catalyst by the combination of methylalumoxane, and alumoxane, i.e., a metallocene catalyst, can be used, for example as the ethylene and an alpha olefin copolymer which carried out the polymerization using the above-mentioned metallocene catalyst. To the active spot of the present catalyst being uneven and being called the multi-site catalyst, since the active spot is uniform, the metallocene catalyst is also called the single site catalyst. Specifically, the ethylene and the alpha olefin copolymer which carried out the polymerization using metallocene catalysts, such as a trade name "affinity (AFFINITY) by the trade name "EKUZAKUTO (EXACT)" by the trade name "a kernel" by Mitsubishi Chemical, Inc., the trade name "EBORYU -" by Mitsui Petrochemical Industries, Ltd., the U.S., and the exon chemical (EXXON CHEMICAL) company, the U.S., and the Dow Chemical Co. (DOW CHEMICAL) and a trade name "engagement (ENGAGE)", can be used.

[0021] ** and in this invention as resin of the ethylene and the alpha olefin copolymer which carried out the polymerization using the above metallocene catalysts It can be used in the condition of the coating film by the constituent containing the film thru/or a sheet, or its copolymer etc. by it It functions as the film thru/or sheet of the resin which has the heat-sealing nature which constitutes an innermost layer, it **, and it becomes possible to prevent generating of the crack produced in the thin film of an inorganic oxide etc. in post processing at the time of bag-making etc. by the low-temperature heat-sealing nature. As thickness of the film or a film thru/or a sheet, 5 micrometers

thru/or about 100 micrometers are desirable preferably 3 micrometers thru/or about 300 micrometers. In this invention, to in addition, the ethylene-alpha olefin copolymer which comes to carry out a polymerization using the above-mentioned metallocene catalyst Furthermore, for example, partial bridge formation ethylene-propylene rubber (EPDM), ethylene-propylene rubber (EPR), A styrene-butadiene-styrene block copolymer (SBS), A styrene-isobutylene-styrene block copolymer (SIS), The heat-sealing nature resin layer by the resin constituent which comes to add more than one sort thru/or it of thermoplastic elastomer, such as a styrene-ethylene-butylene-styrene block copolymer (SEBS), can also be used. moreover, this invention -- setting -- as a heat-sealing nature resin layer -- a line -- the multilayer heat-sealing nature resin layer which consists of a co-extrusion film which uses low density polyethylene and the ethylene-alpha olefin copolymer which comes to carry out a polymerization using a metallocene catalyst, and comes to co-extrude these each is sufficient.

[0022] By the way, in this invention, it combines with the raw material for a package etc. and the arbitration which constitute containers for a package, such as the film of various kinds of resin, a paper base, a metal raw material, a synthetic paper, cellophane, and others, besides the above heat-sealing nature resin layers as plywood concerning this invention, for example, various plywood is manufactured, and manufacture of the plywood suitable for carrying out the restoration package of the various articles in which voile or retorting is possible is enabled. As a film of the above-mentioned resin, specifically For example, low density polyethylene, medium density polyethylene, high density polyethylene, a line -- low density polyethylene, polypropylene, and ethylene propylene rubber -- An ethylene-vinylacetate copolymer, ionomer resin, an ethylene-ethyl-acrylate copolymer, An ethylene-acrylic acid or a methacrylic-acid copolymer, acid denaturation polyolefine system resin, Methylpentene polymer, polybutene system resin, polyvinyl chloride system resin, Polyvinyl acetate system resin, polyvinylidene chloride system resin, a vinyl chloride-vinylidene-chloride copolymer, Pori (meta) acrylic resin, poly acrylic nitril system resin, polystyrene system resin, An acrylonitrile styrene copolymer (AS system resin), acrylonitrile-butadiene-styrene copolymer (ABS system resin), Polyester system resin, polyamide system resin, polycarbonate system resin, It can be used from the film thru/or sheets of well-known resin, such as polyvinyl alcohol system resin, the saponification object of an ethylene-vinylacetate copolymer, fluororesin, diene system resin, polyacetal system resin, polyurethane system resin, a nitrocellulose, and others, being able to choose it as arbitration. In this invention, anythings, such as what was extended by un-extending, one shaft, or 2 shaft orientations, can be used for an above-mentioned film thru/or an above-mentioned sheet. Moreover, the thickness can be used, choosing from the range of several micrometers to about 300 micrometers, although it is arbitrary. Furthermore, in this invention, the film of which descriptions, such as extrusion membrane formation, inflation membrane formation, and coating film, is sufficient as a film thru/or a sheet. Moreover, in the above, paper bases, such as a paper base of ** of strong size nature or non-** or a snow-white roll sheet, kraft paper, the paper board, and a converted paper, others, etc. can be used as a paper base, for example. as the paper base which constitutes paper in the above -- the thing of the 2nd place of basis weight about 80 to 600 g/m -- desirable -- basis weight about 100 to 450 g/m2 It is desirable to use the thing of an about. Moreover, as a metal raw material, the film of the resin which has aluminium foil or the vacuum-plating-of-aluminium film etc. can be used above, for example.

[0023] Next, in above-mentioned this invention, if how to manufacture plywood using the above ingredients is explained, it can carry out by a non-[the approach of laminating usual wrapping for example, a wet lamination process, a dry lamination process, and] solvent mold dry-as approach of starting lamination process, an extrusion lamination process, a T-die extrusion-molding method, the co-extrusion lamination process, the tubular film process, the co-extrusion tubular film process, others, etc. In case it ** and the above-mentioned laminating is performed in this invention, if required For example, corona treatment, ozonization, frame processing, others, etc. can be pretreated on a film. Moreover, for example, a polyester system, an isocyanate system (urethane system), Anchor coating agents, such as a polyethyleneimine system, a poly-butadiene system, and an organic titanium system, Or well-known anchor coat agents, such as adhesives for a lamination, such as a polyurethane system, the Pori acrylic, a polyester system, an epoxy system, a polyvinyl acetate system, a cellulose type, and others, adhesives, etc. can be used.

[0024] Next, in this invention, if bag-making thru/or the approach of carrying out box producing are explained using the above plywood In for example, the case of the soft package bag with which the container for a package consists of a plastic film etc. Use the plywood manufactured by the above

approaches and the field of the heat-sealing nature resin layer of the inner layer is made to counter, it can be turned up, or the two sheets can be piled up, the circumference edge can be heat sealed further, the seal section can be prepared, and a bag body can be constituted. ** and as the bag-making approach [whether the field of the inner layer is made for the above-mentioned complex film to counter, and it bends, and] The two sheets are piled up. Further or the circumference edge of the periphery For example, a side-face seal mold, a two-way-type seal mold, a three-way-type seal mold, a four-way-type seal mold, It can heat seal according to heat-sealing gestalten, such as an envelope **** seal mold, a joining-the-palms-together **** seal mold (pyro-seal mold), a seal mold with a rib, a flat bottom seal mold, a square bottom seal mold, and others, and the container for a package of the various gestalten concerning this invention can be manufactured. In addition to this, it is possible to manufacture for example, a self-standing package bag (standing pouch) etc., and a tube container etc. can be further manufactured in this invention using the above-mentioned complex film. In the above, it can carry out as the approach of heat sealing by well-known approaches, such as a bar seal, revolution low Lucile, BERUTOSHI-RU, impulse heat sealing, a RF seal, and an ultrasonic seal, for example. In addition, in this invention, pour openings, such as for example, a dress type, a two-piece type, and others, or the zipper for closing motion can be attached in the above containers for a package at arbitration.

[0025] Next, as a container for a package, as the case of the liquid restoration form container containing a paper base, for example, plywood, the blank plate which manufactures the layered product which carried out the laminating of the paper base, and manufactures a desired paper carton after this can be manufactured, and box producing of a drum section, a pars basilaris ossis occipitalis, the head, etc. can be carried out after an appropriate time using this blank plate, for example, a paper container for liquid a brick type, a flat type, or gable top type etc. can be manufactured again. Moreover, anythings, such as a paper can of the shape of a cylinder, such as an angle description machine and a round shape, can manufacture the configuration.

[0026] In this invention, the container for a package manufactured as mentioned above It excels in gas barrier property, shock resistance, etc. to transparency, oxygen, a steam, etc. Furthermore, have post-processing fitness, such as lamination, printing processing, bag-making, or box-producing processing, and prevent exfoliation of the thin film of the inorganic oxide as barrier film, and prevent generating of the thermal crack and the degradation is prevented. The resistance which was excellent as barrier film is demonstrated, for example, it excels in the restoration package fitness of various articles, such as chemistry articles, such as an eating-and-drinking article, drugs, a detergent, a shampoo, oil, toothbrushing, adhesives, and a binder, thru/or cosmetics, and others, preservation fitness, others, etc. From the opening, the bag for a package which especially the plywood concerning this invention comes to manufacture bags using it is filled up with contents, seals the opening with heat sealing etc. after an appropriate time, manufactures a package object, subsequently to for example, a retort iron pot can put in this package object, can retort it for 30 minutes 120 degrees C, and can manufacture the retorted package (sterilization processing was carried out) product. Moreover, in the bag for a package which uses the plywood concerning this invention and comes to manufacture bags, the restoration package of the contents can be carried out like the above, a package object can be manufactured, voile processing of this can be carried out the condition for 30 minutes with 90-degree C hot water, and the package product which carried out heat sterilization processing can be manufactured.

[0027]

[Example] Next, an example is given about above-mentioned this invention, and this invention is explained in more detail.

As an example 1(1). base material, the biaxial drawing nylon 6 film (Unitika, Ltd. make) with a thickness of 15 micrometers was used, the moisture-proof paper was stripped, and this was put in into temperature, 90 degrees C, a degree of vacuum, and the vacuum oven of one or less mbar, was left on the 1st, and dehydration processing was performed. Subsequently, the delivery roll of plasma chemistry membrane formation equipment was equipped with the biaxial drawing nylon 6 film which carried out dehydration processing by the above, subsequently to a membrane formation drum, it let out this biaxial drawing nylon 6 film, the thin film of oxidization silicon with a thickness of 140A was formed in the field of one of these on the following plasma chemistry membrane formation conditions, and the barrier property film concerning this invention was manufactured.

(Plasma chemistry vacuum evaporationo conditions)

membrane formation machine: -- roll type plasma chemistry membrane formation machine ultimate-

pressure force: -- 5.0x10-5mbar membrane formation pressure: -- 7.0x10-2mbar line speed: -- 20 m/min power: -- 4kw capacity: -- plasma treatment of the field of the thin film of the oxidation silicon of a barrier property film which manufactured by inert gas 300slm, oxygen gas 300slm, and siloxane gas 100slm vacuum evaporationo die-length:4800m(2)., next the above was carried out on condition that the following. Consequently, the surface tension on the front face of a thin film of oxidation silicon was set to 62dyn from 35dyn, and its wettability improved.
plasma supply-voltage: -- 3kw plasma gas: -- mixed-gas [of helium (helium) and oxygen (O2)] (3) . -- next Use the barrier property film which carried out plasma treatment by the above, and one delivery roll of a dry laminate coating-machine machine is equipped with this. The adhesives layer was formed in the thin film side of the oxidation silicon, the non-extended polypropylene film with a thickness of 40 micrometers which is another side and a sealant film was used, the delivery roll of another side was equipped with this, dry laminate of the both was carried out on condition that the following after an appropriate time, and plywood was manufactured.
Adhesives layer: It is an activity (base resin) urethane system (the Takeda Chemical Industries, Ltd. make, a trade name, TAKENE-TO A-515) about urethane system adhesives.
(Curing agent) Isocyanate system (the Takeda Chemical Industries, Ltd. make, a trade name, A-50)
Base resin: (Mixing ratio) Curing agent =10:1 (solvent) ethyl-acetate (coverage) 4.0 g/m2 (dry cleaning)
In addition, the plywood manufactured above was used, the field of the non-extended polypropylene film was made to counter, and it piled up, and subsequently, the three-way-type seal of the edge of the periphery circumference was carried out, the small bag was manufactured, and it was filled up with the seasoning from opening after an appropriate time, next opening was heat sealed, and the package product was manufactured. The above-mentioned package product was what is excellent in barrier property and is suitable for a prolonged activity.
[0028] As an example 2(1). base material, the moisture-proof paper was stripped, this was put into the drying room which consists of temperature, 40 degrees C, a degree of vacuum, ordinary pressure, humidity, and an absolute dry condition, was left [the biaxial drawing nylon 6 film (Unitika, Ltd. make) with a thickness of 15 micrometers was used,] on the 1st, and dehydration processing was performed. Subsequently, the delivery roll of plasma chemistry membrane formation equipment was equipped with the biaxial drawing nylon 6 film which carried out dehydration processing by the above, subsequently to a membrane formation drum, it let out this biaxial drawing nylon 6 film, the thin film of oxidization silicon with a thickness of 140A was formed in the field of one of these on the following plasma chemistry membrane formation conditions, and the barrier property film concerning this invention was manufactured.
(Plasma chemistry vacuum evaporationo conditions)
membrane formation machine: -- roll type plasma chemistry membrane formation machine ultimate-pressure force: -- 5.0x10-5mbar membrane formation pressure: -- 7.0x10-2mbar line speed: -- 20 m/min power: -- 4kw capacity: -- plasma treatment of the field of the thin film of the oxidation silicon of a barrier property film which manufactured by inert gas 300slm, oxygen gas 300slm, and siloxane gas 100slm vacuum evaporationo die-length:4800m(2)., next the above was carried out on condition that the following. Consequently, the surface tension on the front face of a thin film of oxidation silicon was set to 62dyn from 35dyn, and its wettability improved.
plasma supply-voltage: -- 3kw plasma gas: -- mixed-gas [of helium (helium) and oxygen (O2)] (3) . -- next Use the barrier property film which carried out plasma treatment by the above, and one delivery roll of a dry laminate coating-machine machine is equipped with this. The adhesives layer was formed in the thin film side of the oxidation silicon, the non-extended polypropylene film with a thickness of 40 micrometers which is another side and a sealant film was used, the delivery roll of another side was equipped with this, dry laminate of the both was carried out on condition that the following after an appropriate time, and plywood was manufactured.
Adhesives layer: It is an activity (base resin) urethane system (the Takeda Chemical Industries, Ltd. make, a trade name, TAKENE-TO A-515) about urethane system adhesives.
(Curing agent) Isocyanate system (the Takeda Chemical Industries, Ltd. make, a trade name, A-50)
Base resin: (Mixing ratio) Curing agent =10:1 (solvent) ethyl-acetate (coverage) 4.0 g/m2 (dry cleaning)
In addition, the plywood manufactured above was used, the field of the non-extended polypropylene film was made to counter, and it piled up, and subsequently, the three-way-type seal of the edge of the periphery circumference was carried out, the small bag was manufactured, and it was filled up

with the seasoning from opening after an appropriate time, next opening was heat sealed, and the package product was manufactured. The above-mentioned package product was what is excellent in barrier property and is suitable for a prolonged activity.

[0029] As an example of comparison 1(1). base material, a biaxial drawing nylon 6 film (Unitika, Ltd. make) with a thickness of 15 micrometers is used, and the delivery roll of plasma chemistry membrane formation equipment is equipped with this as it is without carrying out dehydration processing. Subsequently It let out this biaxial drawing nylon 6 film to the membrane formation drum, and to the field of one of these, like the above-mentioned example 1, the thin film of oxidization silicon with a thickness of 140A was formed on the following plasma chemistry membrane formation conditions, and the barrier property film was manufactured.

(Plasma chemistry vacuum evaporationo conditions)

membrane formation machine: -- roll type plasma chemistry membrane formation machine ultimate-pressure force: -- 5.0x10-5mbar membrane formation pressure: -- 7.0x10-2mbar line speed: -- 20 m/min power: -- 4kw capacity: -- plasma treatment of the field of the thin film of the oxidation silicon of a barrier property film which manufactured by inert gas 300slm, oxygen gas 300slm, and siloxane gas 100slm vacuum evaporationo die-length:4800m(2)., next the above was carried out on condition that the following. Consequently, the surface tension on the front face of a thin film of oxidation silicon was set to 62dyn from 35dyn, and its wettability improved.

plasma supply-voltage: -- 3kw plasma gas: -- mixed-gas [of helium (helium) and oxygen (O2)] (3) . -- next Use the barrier property film which carried out plasma treatment by the above, and one delivery roll of a dry laminate coating-machine machine is equipped with this. The adhesives layer was formed in the thin film side of the oxidation silicon, the non-extended polypropylene film with a thickness of 40 micrometers which is another side and a sealant film was used, the delivery roll of another side was equipped with this, dry laminate of the both was carried out on condition that the following after an appropriate time, and plywood was manufactured.

Adhesives layer: It is an activity (base resin) urethane system (the Takeda Chemical Industries, Ltd. make, a trade name, TAKENE-TO A-515) about urethane system adhesives.

(Curing agent) Isocyanate system (the Takeda Chemical Industries, Ltd. make, a trade name, A-50)

Base resin: (Mixing ratio) Curing agent =10:1 (solvent) ethyl-acetate (coverage) 4.0 g/m2 (dry cleaning)

[0030] As an example of comparison 2(1). base material, the biaxial drawing nylon 6 film (Unitika, Ltd. make) with a thickness of 15 micrometers was used, and the moisture-proof paper was stripped, and this was put into 40 degrees C and 90% of thermostatic chamber, and was left for one week. Subsequently, the delivery roll of plasma chemistry membrane formation equipment was equipped with the biaxial drawing nylon 6 film processed above, subsequently to a membrane formation drum, it let out this biaxial drawing nylon 6 film, the thin film of oxidization silicon with a thickness of 140A was formed in the field of one of these on the following plasma chemistry membrane formation conditions, and the barrier property film concerning this invention was manufactured.

(Plasma chemistry vacuum evaporationo conditions)

membrane formation machine: -- roll type plasma chemistry membrane formation machine ultimate-pressure force: -- 5.0x10-5mbar membrane formation pressure: -- 7.0x10-2mbar line speed: -- 20 m/min power: -- 4kw capacity: -- plasma treatment of the field of the vacuum evaporationo thin film of the oxidation silicon of a barrier property film which manufactured by inert gas 300slm, oxygen gas 300slm, and siloxane gas 100slm vacuum evaporationo die-length:4800m(2)., next the above was carried out on condition that the following. Consequently, the surface tension of the vacuum evaporationo thin film front face of oxidation silicon was set to 62dyn from 35dyn, and its wettability improved.

plasma supply-voltage: -- 3kw plasma gas: -- mixed-gas [of helium (helium) and oxygen (O2)] (3) . -- next Use the barrier property film which carried out plasma treatment by the above, and one delivery roll of a dry laminate coating-machine machine is equipped with this. The adhesives layer was formed in the vacuum evaporationo thin film side of the oxidation silicon, the non-extended polypropylene film with a thickness of 40 micrometers which is another side and a sealant film was used, the delivery roll of another side was equipped with this, dry laminate of the both was carried out on condition that the following after an appropriate time, and plywood was manufactured.

Adhesives layer: It is an activity (base resin) urethane system (the Takeda Chemical Industries, Ltd. make, a trade name, TAKENE-TO A-515) about urethane system adhesives.

(Curing agent) Isocyanate system (the Takeda Chemical Industries, Ltd. make, a trade name, A-50)

Base resin: (Mixing ratio) Curing agent =10:1 (solvent) ethyl-acetate (coverage) 4.0 g/m2 (dry cleaning)

[0031] About each barrier property film manufactured in the examples 1-2 and the examples 1-2 of a comparison of the example of experiment 1 above, it carried out in summer (under highly humid), and a winter season (under damp), and the following data were tested 6 times each and measured.

(1) -- measurement of . oxygen transmittance -- about the barrier property film, this is the conditions of the temperature of 23 degrees C, and 90% of humidity RH, and was measured with the measurement machine [a model name and OXTRAN (OXTRAN)] by the U.S. and Mocon (MOCON).

(2) -- measurement of . steam transmittance -- about the barrier property film, this is the conditions of the temperature of 40 degrees C, and 90% of humidity RH, and was measured with the measurement machine [a model name and Palmer tolan (PERMATRAN)] by the U.S. and Mocon (MOCON).

(3) . hole inspection -- this measured the number of through holes formed in a film with the hole test equipment by OMRON Corp. about the barrier property film.

(4) -- the moisture content after . dehydration processing -- this -- the biaxial drawing nylon 6 film after dehydration processing -- the minute amount water measurement machine by Hiranuma Sangyo Co., Ltd. -- using -- Carl Phi Shah -- the moisture content was measured in law.

(5) -- observation of the plasma state under . vacuum evaporationo -- this judged and measured the condition by ROGINGUDE-TA of viewing and a power supply output.

The above-mentioned measurement result is shown in the following tables 1-9.

[0032]

(表1)

(1) . 酸素透過度、夏場

	酸素透過度〔cc/m² ・day・atm〕			
	実施例1	実施例2	比較例1	比較例2
1回目	3．5	4．4	5．1	6．8
2回目	2．9	3．6	4．6	7．7
3回目	4．1	3．6	6．2	7．3
4回目	3．3	4．2	5．6	8．1
5回目	3．2	3．6	6．6	8．2
6回目	4．4	4．7	4．8	7．6
平均	3．6	4．0	5．5	7．6

[0033]

(表2)

(2)．酸素透過度、冬場

	酸素透過度〔cc／m^2・day・atm〕			
	実施例1	実施例2	比較例1	比較例2
1回目	3．4	2．9	4．1	6．6
2回目	2．7	3．1	3．3	6．6
3回目	2．5	3．7	3．5	7．0
4回目	3．9	3．3	3．6	5．9
5回目	2．9	3．7	3．2	6．7
6回目	2．8	2．6	3．1	7．4
平均	3．0	3．2	3．5	6．7

[0034]

(表3)

(3)．水蒸気透過度、夏場

	酸素透過度〔cc／m^2・day・atm〕			
	実施例1	実施例2	比較例1	比較例2
1回目	9．8	12．1	13．2	20．2
2回目	11．0	11．4	14．2	19．4
3回目	10．3	9．9	14．4	16．4
4回目	10．7	11．1	14．5	18．8
5回目	10．5	10．7	13．5	19．9
6回目	8．9	11．0	15．0	18．6
平均	10．2	11．0	14．1	18．9

[0035]

（表４）

（４）．水蒸気透過度、冬場

	酸素透過度〔ｃｃ／ｍ² ・ｄａｙ・ａｔｍ〕			
	実施例１	実施例２	比較例１	比較例２
１回目	１１．１	１１．９	１０．７	１９．９
２回目	１０．７	１１．８	１２．１	２０．７
３回目	９．９	１２．１	１１．８	１８．９
４回目	１１．０	９．９	１２．０	２０．１
５回目	１０．２	１０．９	１１．５	１９．６
６回目	１０．２	１０．６	１３．０	１９．３
平均	１０．５	１１．２	１１．９	１９．８

[0036]

（表５）

（５）．穴検査、夏場

	穴　〔個／１１ｏｔ〕			
	実施例１	実施例２	比較例１	比較例２
１回目	0	0	1	2
２回目	0	0	0	1
３回目	0	0	0	0
４回目	0	0	0	1
５回目	0	0	1	1
６回目	0	0	0	1
平均	0	0	0．３	1

[0037]

（表６）
（６）．穴検査、冬場

	穴　〔個／１１ｏｔ〕			
	実施例１	実施例２	比較例１	比較例２
１回目	０	０	０	１
２回目	０	０	０	０
３回目	０	０	１	２
４回目	０	０	０	１
５回目	０	０	０	２
６回目	０	０	０	２
平均	０	０	０．２	１．３

[0038]
（表７）
（７）．水分量、夏場

	水分量〔　％　〕			
	実施例１	実施例２	比較例１	比較例２
１回目	０．４５	０．４４	１．８７	２．７０
２回目	０．４１	０．４３	１．６８	２．７８
３回目	０．４２	０．４３	１．７８	２．９１
４回目	０．３９	０．５０	１．８０	２．７９
５回目	０．４１	０．４５	１．７６	２．８４
６回目	０．４２	０．４０	１．８６	２．８３
平均	０．４２	０．４４	１．７９	２．８１

[0039]

(表8)
(8). 水分量、冬場

	水分量〔 % 〕			
	実施例1	実施例2	比較例1	比較例2
1回目	0. 41	0. 42	1. 33	2. 66
2回目	0. 38	0. 41	1. 51	2. 76
3回目	0. 38	0. 43	1. 22	2. 65
4回目	0. 44	0. 41	1. 54	2. 89
5回目	0. 38	0. 45	1. 34	2. 51
6回目	0. 40	0. 42	1. 50	2. 65
平均	0. 40	0. 42	1. 41	2. 69

[0040]
(表9)
(9). プラズマ状態(目視)

	夏場		冬場	
	皺状態	プラズマ状態	皺状態	プラズマ状態
実施例1	○	○	○	○
実施例2	○	○	○	○
比較例1	×	×	△	○
比較例2	××	××	××	××

the above-mentioned table -- setting -- the inside of the column of a wrinkle condition, and O -- wrinkle nothing and ** -- a wrinkle a few -- generating and x -- wrinkling and xx -- a wrinkle -- many generating is meant. Moreover, in the above-mentioned table, O means stability among the column of the plasma state, and, as for x, instability and xx mean instability considerably.
[0041] (10) About the thing of . plasma state examples 1-2 and the examples 1-2 of a comparison, 6 times, although six winter seasons were measured, what graph-ized EP applied voltage value data for the 1st plasma state summer (ROGINGUDE-TA) is shown in drawing 4 , drawing 5 , drawing 6 , and drawing 7 summer.
[0042] When dehydration processing was carried out before membrane formation in this invention, it has checked that barrier property improved, so that clearly from the above-mentioned measurement result. Since moisture degasifying is controlled from a biaxial drawing polyamide system resin film (membrane formation side) during membrane formation, this is because there was no membrane formation molecule coat formation inhibition. Moreover, in this invention, when dehydration processing was carried out before membrane formation, it has checked that the formation of wrinkles was lost and the plasma was stabilized. Since moisture degasifying from a biaxial drawing polyamide system

resin film (a rear face, field non-forming membranes) is controlled during membrane formation, the float and the formation of wrinkles of a film of this are lost, and it is because the plasma was stabilized. As mentioned above, in this invention, when dehydration processing was performed to the biaxial drawing polyamide system resin film before membrane formation, it has checked that there was effectiveness in barrier property, plasma stability, etc.

[0043]

[Effect of the Invention] By the above explanation, as for this invention, dehydration processing of the biaxial drawing polyamide system resin film is carried out before membrane formation of the thin film of an inorganic oxide so that clearly, And the plasma chemistry forming-membranes method is rich in flexibility, flexibility, flattery nature, etc. in comparison. It notes being able to form the thin film of the inorganic oxide which can control generating of a crack etc. first a biaxial drawing polyamide system resin film For example, vacuum oven, Dehydration processing is carried out in the drying room of an absolute dry condition etc., and the water content after dehydration processing of a biaxial drawing polyamide system resin film is prepared to 0.3% - 0.7% (weight fraction) before membrane formation of the thin film of an inorganic oxide. Or subsequently To one field of this biaxial drawing polyamide system resin film, by the plasma chemistry forming-membranes method The thin film of inorganic oxides, such as oxidization silicon, is prepared, a barrier property film is manufactured, a heat-sealing nature resin layer etc. is further prepared in the thin film side of the inorganic oxide of this barrier property film at least, and plywood is manufactured. Subsequently Use this plywood, manufacture this and manufacture the container for a package, and after an appropriate time, carry out the restoration package of the contents into this container for a package, and further, heat seal the opening and a package object is manufactured. Most phenomena in which moisture etc. comes up from a biaxial drawing polyamide system resin film at the time of membrane formation of the thin film of inorganic oxides, such as oxidation silicon, cannot be accepted. And the effect does not exist, either and the thin film of inorganic oxides, such as oxidation silicon, can be membrane-formation-ized very good on the front face of this polyamide system resin film. And it excels in the adhesion of this biaxial drawing polyamide system resin film and the thin film of inorganic oxides, such as oxidation silicon. Consequently, it has the very high barrier property to oxygen gas or a steam. And the plywood which was excellent in transparency, and was excellent in lamination reinforcement etc. further, for example, used a useful barrier property film and useful it for carrying out the restoration package of the various articles, such as an eating-and-drinking article, drugs, cosmetics, a chemistry article, and others, can be manufactured.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the rough sectional view showing the lamination of the example about the barrier property film concerning this invention.
[Drawing 2] It is the rough sectional view showing the lamination of the example about the plywood which used the barrier property film concerning this invention.
[Drawing 3] It is the rough block diagram of the plasma chemistry membrane formation equipment which illustrates the example about the manufacturing method of the barrier property film concerning this invention.
[Drawing 4] It is the graph which shows the plasma state (ROGINGUDE-TA) about a barrier property film.
[Drawing 5] It is the graph which shows the plasma state (ROGINGUDE-TA) about a barrier property film.
[Drawing 6] It is the graph which shows the plasma state (ROGINGUDE-TA) about a barrier property film.
[Drawing 7] It is the graph which shows the plasma state (ROGINGUDE-TA) about a barrier property film.
[Description of Notations]
A Barrier property film
B Plywood
1 Biaxial Drawing Polyamide System Resin Film
2 Thin Film of Inorganic Oxide
3 Heat-Sealing Nature Resin Layer
11 Plasma Chemistry Membrane Formation Equipment
12 Vacuum Chamber
13 It Begins to Wind and is Roll.
14 Guy Delors
15 Membrane Formation Drum
16, 17, 18 Raw material volatilization feeder
19 Feeding Nozzle
20 Glow Discharge Plasma
21 Power Source
22 Magnet
23 Guy Delors
24 Rolling-Up Roll
25 Vacuum Pump

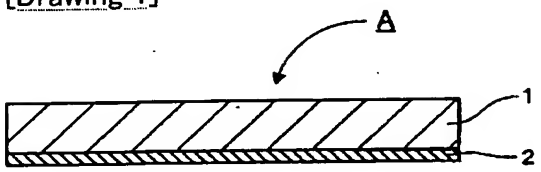
[Translation done.]

* NOTICES *

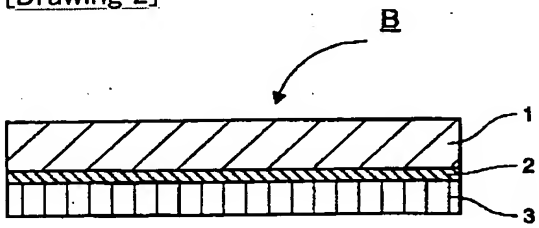
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

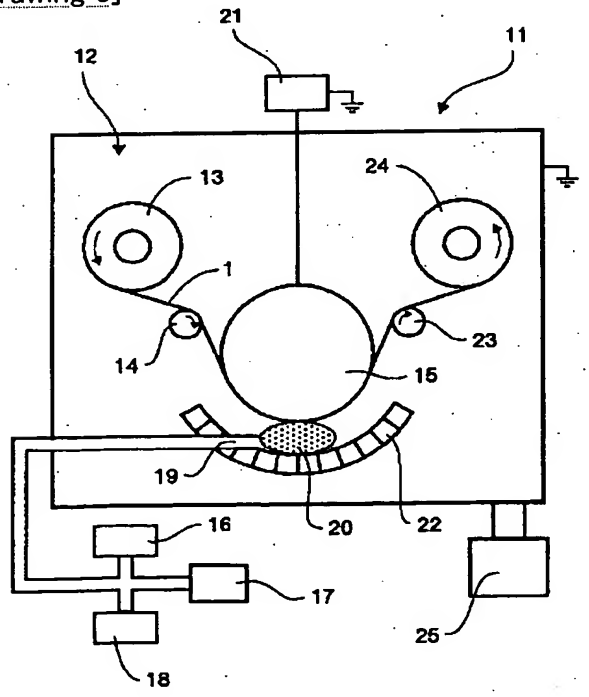
[Drawing 1]



[Drawing 2]

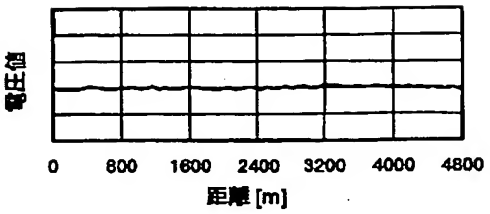


[Drawing 3]



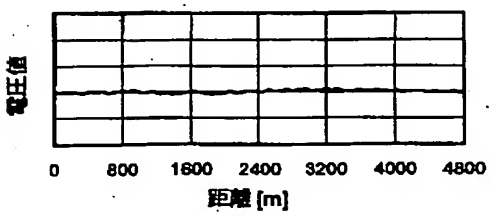
[Drawing 4]

実施例１（電圧値）



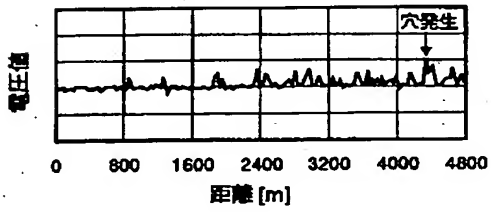
[Drawing 5]

実施例２（電圧値）



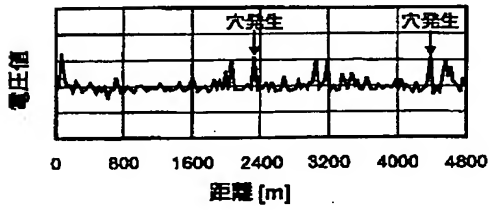
[Drawing 6]

比較例１（電圧値）



[Drawing 7]

比較例２（電圧値）



[Translation done.]